Title:

Renewable diesel production from rapeseed oil with hydrothermal hydrogenation and subsequent decarboxylation

Authors: Yuitsu Sugami, Eiji Minami and Shiro Saka

Affiliation: Graduate School of Energy Science, Kyoto University, Japan

Address: Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Tel/Fax: +81 (0) 75 753 4738

E-mail: saka@energy.kyoto-u.ac.jp

Corresponding author: Shiro Saka

Highlights

- Hydrocarbon production from rapeseed oil was studied.
- The process consists of hydrolysis/hydrogenation and subsequent decarboxylation.
- The composition of the obtained hydrocarbons can be foreseen from raw material.
- The product meets the Japanese diesel standard by blending with fossil diesel.

Abstract

Hydrocarbon (renewable diesel) production from rapeseed oil was studied with hydrothermal hydrogenation and subsequent decarboxylation in a batch-type reaction vessel. An appropriate reaction condition for hydrothermal hydrogenation was found to be 270 ºC/ 5 MPa (H_2 pressure) with water and Pd/C catalyst for 60 min, under which triglycerides were simultaneously hydrolyzed and hydrogenated into saturated fatty acids in a yield of 98.4 mol%. The obtained saturated fatty acids were then decarboxylated to hydrocarbons under the condition of 300 ºC/ 1 MPa (H_2 pressure) with Pd/C for 120 min in a yield of 91.5 mol% on rapeseed oil. In addition, the composition of the obtained hydrocarbons corresponded nearly to that of the fatty acid in rapeseed oil. Such a result indicates that the composition of hydrocarbons produced in this proposed process can be foreseen from fatty acid composition of the feedstock triglycerides. By blending the obtained hydrocarbons from rapeseed oil with an adequate amount of fossil diesel, the blended fuel could satisfy the specification standard of fossil diesel in Japan.

Keywords

Renewable diesel; Plant oil; Hydrolysis; Hydrogenation; Decarboxylation

1. Introduction

The fossil fuels are finite resources and their mass consumption has significant impacts on our environment and society. For these reasons, fatty acid methyl ester (FAME) is being used as an alternative diesel fuel produced by transesterification of triglyceride, a main component of plant oil, with methanol. Because FAME is renewable fuel containing no aromatics and sulfur, it can reduce exhaust emissions [1, 2]. However, FAME has some drawbacks caused by the difference in chemical structure from petroleum diesel, for example, corrosiveness against certain types of rubber and metal [3] and poor oxidation stability due to unsaturated double bonds [1-4]. To overcome such drawbacks, hydrocarbon productions from plant oils with the hydrotreating and catalytic cracking are being researched worldwide [5-19].

The hydrotreatment of plant oils was usually studied in the temperature range between 350 and 450 ºC under the pressure between 4 and 15 MPa with H_2 and a catalyst [5-13]. As a catalyst, for example, sulfided CoMo and NiMo supported on SiO_2, Al_2O_3, ZrO_2, TiO_2 and zeolites were used [5-11]. Under the hydrotreating reaction, first, double bonds in fatty acid moieties of triglyceride are hydrogenated into saturated C-C bonds, followed by the cleavage of ester linkages to produce one molecule of propane and three molecules of saturated fatty acids [6, 12]. The obtained saturated fatty acids are then deoxidized into hydrocarbons having carbon numbers mainly between 15 and 18 through hydrodeoxygenation, decarbonylation and decarboxylation [8, 13]. This reaction also produces *i*-paraffin and naphthene through isomerization and cyclization of olefin intermediates, which

39 contributes to improving the cold-flow properties. In addition, CO, CO_2, H_2O and propane are
40 produced as byproducts [6].

41 On the other hand, the catalytic cracking of plant oils was usually carried out in the
42 temperature range between 300 and 500 ºC under atmospheric pressure with zeolites, Al_2O_3 and MgO
43 as a catalyst [14-17], under which the thermal decomposition is predominant. First, triglycerides are
44 decomposed to fatty acids, ketones, aldehydes and esters [18]. These products undergo secondary
45 cracking to form short and long chain paraffins and olefins with CO, CO_2, H_2O and alcohols by
46 breaking C-O and C-C bonds via decarboxylation and decarbonylation. However, this process makes
47 various hydrocarbons having wide range of carbon numbers with olefins and aromatics.

48 After all, the selectivity of the products is not so high with the conventional hydrotreating and
49 catalytic cracking mentioned above. It should be caused by the presence of unsaturated fatty acid
50 moieties, which leads to various side reactions. Actually, Dos Anjos et al. studied the catalytic cracking
51 of prehydrogenated soybean oil as well as crude one, reporting that prehydrogenated oil yielded
52 essentially pure hydrocarbon products, while crude oil yielded a mixture of oxygen-containing products
53 and the lower molecular weight hydrocarbons [20].

54 In this study, therefore, hydrocarbon production from plant oil was studied through two-step
55 reaction with hydrolysis and subsequent decarboxylation. During the hydrolysis step, hydrogenation
56 was simultaneously conducted to produce stable saturated fatty acids, which may suppress undesirable
57 side reactions during subsequent decarboxylation [19, 20]. In the literature [5-21], furthermore, an

organic solvent such as *n*-dodecane was usually added to enhance the fluidity of the reactants and to avoid the deactivation of catalyst, even though only a few studies without any solvent can be found [19, 22]. However, the use of such organic solvent requires additional separation and purification steps after the reaction, and it makes the whole process complicated. Therefore, the reactions of this study were conducted without any organic solvent so as to simplify the process for production of hydrocarbons as renewable diesel.

2. Materials and Methods

2.1. Experimental procedures

Fig.1 shows the schematic diagram of the saturated hydrocarbon (renewable diesel) production process in this study via saturated fatty acids from rapeseed oil. Prior to the experiment, Pd/C catalyst (Pd/C = 5/95 (w/w), Nacalai Tesque, Inc.) was dried overnight at 105 ºC and reduced in H_2 flow (15 ml/min) at 200 ºC for 60 min. Rapeseed oil (reagent grade, Nacalai Tesque, Inc.) was, then, treated in hot-compressed water with H_2 gas and Pd/C catalyst for hydrolysis and hydrogenation to obtain saturated fatty acids. The obtained saturated fatty acids were then decarboxylated with Pd/C catalyst to produce saturated hydrocarbons by decarboxylation.

2.1.1. Hydrolysis coupled with hydrogenation (Hydrolysis/hydrogenation)

A batch-type reaction vessel (inner volume: 5.0 ml) made of Inconel-625 [23] was used for the reaction. One gram of rapeseed oil and 1.0 - 3.0 g of ion-exchanged water were placed into the reaction vessel with 0.05 g of Pd/C. Hastelloy balls (total volume: 0.2 ml) were also placed into the vessel to agitate the mixture efficiently. After the vessel was sealed, the inside of the vessel was purged and pressurized to 5 MPa with H_2 gas using a gas-supplying system. The hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation) reaction was then conducted by immersing the vessel into a molten salt bath preheated at 270 ºC, which is the optimum temperature for hydrolysis of triglycerides found in previous works [24, 25]. The reaction vessel was swung from side to side to agitate the mixture during the reaction. After a designated treatment time, the vessel was moved into a water bath to quench the reaction. The obtained reaction mixture dissolved in tetrahydrofuran (THF, specially prepared reagent grade, Nacalai Tesque, Inc.) was, then, taken out from the vessel, sonicated for 30 min, and the catalyst was removed with a filter paper in a micropore of 0.45 μm (Merck Millipore Co.). The products were, then, warmed up in a water bath at 70 ºC for 30 min and separated into THF and water phases. By removing THF from the THF phase with a rotary vacuum evaporator, the products of the hydrolysis/hydrogenation reaction were collected and their yield was determined.

2.1.2. Decarboxylation

For subsequent decarboxylation, approximately 0.9 g of the obtained saturated fatty acids and 0.05 - 0.45 g of Pd/C were placed into the 5 ml reaction vessel with Hastelloy balls. The inside of the reaction vessel was then purged and pressurized with N_2 or H_2 gas to be 1 MPa which is a favorable pressure for decarboxylation reaction [26]. The decarboxylation was, then, conducted with the molten salt bath at 300 ºC for 120 min, which is an appropriate condition reported by Lestari *et al*. [27], and quenched into the water bath in the same way mentioned above. After the reaction, the obtained products dissolved in THF were taken out from the vessel, sonicated for 30 min, and the catalyst was removed with the filter paper. After removing THF by the evaporator, the decarboxylated products were obtained to determine its yield. To clarify the decarboxylation reaction of the saturated fatty acid, palmitic acid, stearic acid and arachidic acid (all being guaranteed reagent grade from Nacalai Tesque, Inc.) were also studied.

2.2. Analytical methods

The fatty acid composition of rapeseed oil used in this work was determined in accordance with the Japan Oil Chemists' Society standard method [28]. The products, obtained from hydrolysis/hydrogenation and subsequent decarboxylation, were analyzed by gel permeation chromatography (GPC, Shimadzu Co. LC-10VP system, column: GF-310 HQ (Showa Denko K.K.), oven temperature: 40 ºC, mobile phase: THF, flow-rate: 1.0 ml/min, detector: refractive index detector

RID-10A) and high performance liquid chromatography (HPLC, column: Cadenza CD-C18 (Imtakt Co.), oven temperature: 40 ºC, mobile phase: methanol, flow-rate: 1.0ml/min, detector: RID-10A). By the GPC analysis, the obtained products from hydrolysis/hydrogenation can be separated into four peaks, which correspond to the groups of triglycerides, diglycerides, monoglycerides and fatty acids. The amount of each group was quantified based on the corresponding peak area, using tristearin, 1,3-distearin, 1-monostearin (all being >99% grade from Olbracht Serdary Research Laboratories) and stearic acid (guaranteed reagent grade from Nacalai Tesque, Inc.) as calibration standards. The HPLC analysis, by which fatty acids can be separated into single ones, was then conducted to quantify the amount of each fatty acid. In this way, the yields of the products were determined in mol%. The obtained product from the decarboxylation reaction was also quantified in a similar manner.

The fuel properties of the renewable diesel were evaluated for flash point, pour point, cold filter plugging point, kinematic viscosity and density as in Table 2. In addition, the renewable diesel was blended in various ratios with fossil diesel (#1 diesel of the Japanese Industrial Standard (JIS), purchased from SHOWA SHELL SEKIYU K.K.), and their fuel properties were also evaluated. The density was determined in accordance with the ASTM International's standard ASTM D1298 [29], while the flush point, pour point, cold filter plugging point and kinematic viscosity were measured by the automated Pensky-Martens closed cup flush point tester (APM-7), the mini pour point tester (MPC-102), the automated cold filter plugging point tester (AFP-102) and the automatic kinematic viscosity measuring system (AKV-201), respectively. All of these measuring systems were made by

Tanaka Scientific Co. Ltd. The acid and iodine values were determined in accordance with ASTM D974 and D1959 [30, 31].

3. Results and Discussion

Table 1 shows the fatty acid composition of rapeseed oil and yields of the products obtained after hydrolysis/hydrogenation and subsequent decarboxylation. Rapeseed oil used in this study is composed of saturated and unsaturated fatty acids with 16, 18 and 20 carbon atoms. Through this study, appropriate reaction conditions for hydrolysis/hydrogenation and decarboxylation were evaluated as described in the following subsections.

3.1. Hydrolysis/hydrogenation

Figure 2(a) and 2(b) show respectively GPC and HPLC chromatograms of the obtained products through hydrolysis/hydrogenation reaction from 0.9 g of rapeseed oil as treated at 270 ºC/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C. In Fig. 2(a), triglycerides (TG) in rapeseed oil are decreasing as reaction time is prolonged. For 20 and 40 min treatments, diglycerides (DG) and monoglycerides (MG) are being observed as intermediate compounds, but almost all of them also disappear after 60 min. Meanwhile, fatty acids (FA) are increasing with reaction time until 60 min treatment. Incidentally, the retention time of triglycerides in the GPC chart shifts slightly to the shorter retention time after 20 min treatment. It would imply that the double bonds in fatty acid moieties are

converted into saturated ones through hydrogenation, because saturated fatty acids have a slightly shorter retention time than unsaturated ones on the GPC column used in this study. Actually, only saturated fatty acids such as palmitic ($C_{16:0}$), stearic ($C_{18:0}$) and arachidic ($C_{20:0}$) acids can be found after 20 min treatment by HPLC analysis as shown in Fig. 2(b). It indicates that hydrogenation is faster than hydrolysis and completed within 20 min.

From the above, an appropriate reaction time for hydrolysis/hydrogenation was found to be 60 min at the given conditions. Based on the HPLC and GPC analyses, the yield of the products from rapeseed oil was determined as shown in Table 1. Triglycerides in rapeseed oil were converted into saturated fatty acids and their yield was summed up to be 96.1 (= 4.5 + 89.7 + 1.9) mol%. In addition, 2.3 mol % of glycerides still remained as intermediate compounds. Finally, the total yield of fatty acids and glycerides was 98.4 mol% and any other products were not observed in the HPLC chart. In addition, no gaseous products were produced and saturated fatty acids are stable under the given condition. Thus, no product decomposition would be occurred. Therefore, the rest of 1.6 mol% would probably be lost through the purification steps. By excluding the lost portion, the molar ratio upon the obtained products basis was shown in parenthesis in Table 1. As a result, the molar ratio of the obtained saturated fatty acids ($C_{16:0}$: $C_{18:0}$: $C_{20:0}$ = 4.6 : 91.2 : 1.9) is close to the fatty acid composition of rapeseed oil ($C_{16:0}$ + $C_{16:1}$: $C_{18:0}$ + $C_{18:1}$ + $C_{18:2}$ + $C_{18:3}$: $C_{20:0}$ + $C_{20:1}$ = 4.5 : 94.0 : 1.5). It means that the selective reaction to be saturated fatty acids has occurred during the hydrolysis/hydrogenation step.

With regard to the amount of water, on the other hand, 1.0 g of rapeseed oil was hydrolyzed with 3.0 g of water. Thus, the weight ratio of water/rapeseed oil was 3.0/1.0 for Table 1 and Fig. 2. However, when its ratio decreased from 3.0/1.0 to 1.0/1.0, the yield of saturated fatty acids decreased from 97.7 mol% to 77.2 mol% due to the insufficient hydrolysis of glycerides and fatty acids under the same reaction condition. From these results, it was concluded that an appropriate hydrolysis/hydrogenation condition is 270 ºC/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C for 1.0 g of rapeseed oil.

3.2. Decarboxylation

As a preliminary experiment, the effect of atmospheric gas (N_2 or H_2) was investigated on decarboxylation reaction by using stearic acid as a model compound. When N_2 gas was used, no conversion was observed at the conditions of 300 ºC/ 1 MPa/ 0.05 g of Pd/C for 120 min. In the case of H_2 gas, on the other hand, 16.3 mol% of *n*-heptadecane was obtained at the same condition. Although H_2 is not essentially required by the decarboxylation reaction, it keeps the catalyst activity [32, 33]. Actually, some researchers have reported that an efficient decarboxylation was observed in the presence of H_2 [19, 33, 34]. Therefore, H_2 gas was used in the following experiments.

Moreover, decarboxylation reaction was carried out for 0.9 g of stearic acid as a model compound to determine an appropriate amount of the catalyst at the conditions of 300 ºC/ 1 MPa (H_2) for 120 min. When the two different amounts of Pd/C were studied to be 0.05 and 0.25 g, incomplete

conversions were found respectively to be 16.3 and 26.1 mol% from stearic acid into *n*-heptadecane. On the other hand, 90.3 mol% of *n*-heptadecane was achieved with 0.45 g of Pd/C. Therefore, it was concluded that 0.45 g of Pd/C is required for the efficient decarboxylation of 0.9 g of fatty acid at the given conditions. In general, decarboxylation of fatty acids proceeds in three phases, gaseous H_2, liquid fatty acids and a solid catalyst, in which the mutual accessibility is an important factor. Although an organic solvent is usually added to improve its accessibility in the literature [21], decarboxylation was conducted without any organic solvent in this study to simplify the reaction process. That might be the reason why such a large amount of Pd/C catalyst was needed. Therefore, an effective agitation would be required to reduce the amount of the catalyst.

On the other hand, Fig.3 shows HPLC chromatograms of rapeseed oil, the obtained fatty acids by hydrolysis/hydrogenation and hydrocarbons after decarboxylation. Triglycerides in rapeseed oil are composed of various fatty acids, thus many peaks are found in Fig.3. However, these peaks are converted mainly into three peaks of saturated fatty acids, palmitic ($C_{16:0}$), stearic ($C_{18:0}$) and arachidic ($C_{20:0}$) acids, by hydrolysis/hydrogenation of triglycerides. These saturated fatty acids are then converted into *n*-pentadecane ($C_{15}H_{32}$), *n*-heptadecane ($C_{17}H_{36}$) and *n*-nonadecane ($C_{19}H_{40}$), respectively, by subsequent decarboxylation. Therefore, the obtained renewable diesel from rapeseed oil consists of these three kinds of saturated hydrocarbons.

Based on the HPLC and GPC analyses, the yields of hydrocarbons were determined as shown in Table 1. The total yield of hydrocarbons was 91.5 mol% and any other products were not observed.

205 Since hydrocarbons are stable enough under the given condition, no decomposition of the products can
206 be occurred. Therefore, the rest of 8.5 mol% would probably be lost through the purification steps. The
207 loss of the products would be caused by using a large amount of catalyst, on which the products were
208 adsorbed. The molar ratio upon the obtained hydrocarbon basis was shown in parenthesis in Table 1. As
209 a result, the molar ratio of obtained *n*-pentadecane, *n*-heptadecane and *n*-nonadecane was found out to
210 be 4.5 : 93.6 : 1.9. This molar ratio is nearly close to the one of saturated fatty acids ($C_{16:0}$: $C_{18:0}$: $C_{20:0}$
211 = 4.6 : 91.2 : 1.9 in Table 1) obtained after hydrolysis/hydrogenation. Therefore, these saturated fatty
212 acids seem to be selectively converted without any side reaction into the corresponding hydrocarbons
213 through decarboxylation. In case of unsaturated fatty acids, however, various side reactions such as
214 hydrogenation, dehydrogenation, cyclization, ketonization, dimerization and cracking have been
215 reported to occur concurrently due to the unstable double bonds present [35, 36], which lead to
216 decrease the degree of the specific production of hydrocarbons. Therefore, unsaturated fatty acids
217 should be converted into saturated ones before decarboxylation to maintain its high selectivity. For this
218 specificity, the process shown in Fig. 1 is appropriate and promising.

219 After hydrolysis/hydrogenation, 2.3 mol% of glycerides such as monoglycerides and
220 diglycerides still remain as shown in Table 1. However, these intermediate compounds are disappeared
221 after decarboxylation, and converted into hydrocarbons. Actually, when 1-monostearin was treated at
222 the same condition, it was converted into *n*-heptadecane by decarboxylation treatment with H_2 gas and
223 Pd/C catalyst even though the reactivity was slightly low, compared with saturated fatty acids.

Therefore, the remaining glycerides must be converted to saturated fatty acids during decarboxylation treatment.

The iodine and acid values of the obtained hydrocarbons from rapeseed oil were evaluated and found out to be zero. This means that the obtained products have neither double bonds nor fatty acids. It is, therefore, evident that hydrogenation and decarboxylation reactions are successfully completed during the process.

3.3. Fuel properties of saturated hydrocarbons

It is very important to evaluate the fuel properties of the renewable diesel. However, the prepared renewable diesel is not sufficient in amount to test the fuel properties. As in Table 1, it consists of the saturated linear hydrocarbons of *n*-pentadecane, *n*-heptadecane and *n*-nonadecane in a molar ratio of 4.5 : 93.6 : 1.9. In addition, it was confirmed that such a mixture does not contain any contaminants. Therefore, a mixture of these three kinds of hydrocarbons was prepared from their chemicals purchased as the renewable diesel and evaluated for the fuel properties.

Table 2 shows the evaluated fuel properties of the mixtures of renewable diesel with #1 fossil diesel in various ratios. In case of 100 vol% renewable diesel, it has a higher flash point than that of the fossil diesel (0 vol% renewable diesel in Table 2), and satisfies the specification standard of the fossil diesel in Japan (JIS K2204) [37]. Such a property should be originated from *n*-heptadecane, a main component of the fuel, which has a relatively high boiling point among the hydrocarbons in petroleum

243 diesel. In addition, the values of kinematic viscosity and density also satisfy the requirements for the
244 Japanese diesel standard. These values are also close to the ones of *n*-heptadecane. On the other hand,
245 the cold-flow properties such as pour point and cold filter plugging point are poor due to the presence
246 of saturated linear hydrocarbons, because these have relatively high melting points, especially in case
247 of *n*-heptadecane. Therefore, the cold-flow properties should be improved to meet the fossil diesel
248 standard. Blending the renewable diesel with fossil one is a simple way for this purpose. In case of 20
249 vol% renewable diesel, as shown in Table 2, the pour point and cold filter plugging point are improved,
250 and thus, it can satisfy the requirements for the fuel standard. However, when the ratio of renewable
251 diesel is increased to be 30 vol%, the pour point exceeds the limit of the standard. From such a reason,
252 the blending ratio would be limited up to around 20 vol% to meet all requirements of the specification
253 standard in Table 2. This further indicates that the obtained hydrocarbons through this process can be
254 used as renewable diesel by blending with fossil diesel.
255
256 **4. Concluding Remarks**
257 To produce hydrocarbons from plant oil as renewable diesel fuel, the conventional
258 hydrotreating and catalytic cracking processes are not really specific for the products selectivity due to
259 unsaturated double bonds. In this study, therefore, the process composed of hydrolysis/hydrogenation
260 and subsequent decarboxylation was proposed. In the first treatment, triglycerides in rapeseed oil were
261 converted into saturated fatty acids through hydrolysis in hot-compressed water and simultaneous

hydrogenolysis under the presence of Pd/C catalyst and H_2 gas. In the second treatment, the obtained saturated fatty acids were decarboxylated into the corresponding hydrocarbons under the presence of Pd/C. In this process, unsaturated double bonds in fatty acid moieties, which lead to various side reactions, were hydrogenated into saturated ones prior to the second treatment. Therefore, the selective conversion was achieved by this two-step treatment without any side reaction. As a result, the composition of the obtained hydrocarbons corresponded to the fatty acid composition of rapeseed oil.

However, the obtained renewable diesel fuel should be improved in cold-flow properties because saturated linear hydrocarbons have relatively high melting points, whereas other properties such as flash point, kinematic viscosity and density satisfied the requirements of the fossil diesel. To satisfy the requirements, a blend of renewable diesel with fossil diesel was found out to weaken the inferior fuel properties of pour point and cold filter plugging point. Consequently, 20 vol% blend of the renewable diesel was found out to satisfy the requirements for the Japanese specification standard of the fossil fuel.

Acknowledgement

This work was supported by a Grant-in-Aid for Challenging Exploratory Research (No. 25660279, 2013.4-2014.3), supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] Krawcyk T. BIODIESEL: alternative fuel makes inroads but hurdles remain. Inform 1996;7(8):801-15

[2] Knothe G, Sharp CA, Ryan TW. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. Energ Fuel 2006;20(20):403–8.

[3] Haseeb ASMA, Fazal MA, Jahirul MI, Masjuki HH. Compatibility of automotive materials in biodiesel: A review. Fuel 2011;90(3):922-31.

[4] Moser BR. Biodiesel production, properties, and feedstocks, In Vitro Cell Dev–Pl 2009;45(3):229-66.

[5] Monnier J, Tourigny G, Soveran DW, Alfred Wong, Hogan EN, Stumborg M. Conversion of biomass feedstock to diesel fuel additive, US patent 5705722, 1998.

[6] Satyarthi JK., Chiranjeevi T, Gokak DT, Viswanathan PS. An overview of catalytic conversion of vegetable oils/fats into middle distillate. Catal Sci Technol 2013;3(1):70-80.

[7] Gong S, Shinozaki A, Shi M, Qian EW. Hydrotreating of Jatropha Oil over Alumina Based Catalysts. Energ Fuel 2012;26(4):2394−9.

[8] Kubička D, Kaluža L. Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts. Appl Catal A: Gen 2010;372(2):199–208.

[9] Madsen AT, Ahmed EH, Christensen CH, Fehrmann R, Riisager A. Hydrodeoxygenation of waste fat for diesel production: Study on model feed with Pt/alumina catalyst. Fuel 2011;90(11):3433–8.

299 [10] Krár M, Kovács S, Kalló D, Hancsók J. Fuel purpose hydrotreating of sunflower oil on
300 $CoMo/Al_2O_3$ catalyst. Bioresource Technol 2010;101(23):9287–93.
301 [11] Huber GW, O'Conno P, Corma A. Processing biomass in conventional oil refineries: Production of
302 high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. Appl Catal A:
303 Gen 2007;329(1):120–9.
304 [12] Watanabe M, Iida T, Inomata H. Decomposition of a long chain saturated fatty acid with some
305 additives in hot compressed water. Energ Convers Manage 2006;47(18-19):3344-50.
306 [13] Mikulec J, Cvengroš J, Joríková Ľ, Banič M, Kleinová A. Second generation diesel fuel from
307 renewable sources. J Clean Prod 2010;18(9):917–26.
308 [14] Tani H, Shimouchi M, Haga H, Fujimoto K. Development of Direct Production Process of Diesel
309 Fuel from Vegetable Oils. J Jpn Inst Energy 2011;90:466-70.
310 [15] Maher KD, Bressler DC. Pyrolysis of triglyceride materials for the production of renewable fuels
311 and chemicals. Bioresource Technol 2007;98(12):2351–68.
312 [16] Rao KVC. Production of hydrocarbons by thermolysis of vegetable oils. US patent 4102938 A,
313 1978.
314 [17] Twaiq FA, Zabidi NAM, Bhatia S. Catalytic Conversion of Palm Oil to Hydrocarbons:
315 Performance of Various Zeolite Catalysts. Ind Eng Chem Res 1999;38(9):3230-7.
316 [18] Taufiqurrahmi N, Bhatia S. Catalytic cracking of edible and non-edible oils for the production of
317 biofuels. Energy Environ Sci 2011;4:1087-112.

318 [19] Snåre M, Kubičková I, Mäki-Arvela P, Chichova D, Eränen K, Murzin DY. Catalytic
319 deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons.
320 Fuel 2008;87(6):933-45.
321 [20] Dos Anjos JRS, Gonzalez WDA, Lam YL, Frety R. Catalytic decomposition of vegetable oil. Appl
322 Catal 1983;5(3):299-308.
323 [21] Wang WC, Thapaliya N, Campos A, Stikeleather LF, Roberts WL. Hydrocarbon fuels from
324 vegetable oils via hydrolysis and thermo-catalytic decarboxylation. Fuel 2012;95:622-9.
325 [22] Theilgaard MA, Rosmyslowicz B, Mäki-Arvela P, Simakova IL, Eränen K, Murzin DY, Fehrmann,
326 R., Deactivation in Continuous deoxygenation of C18-fatty feedstock over Pd/Sibunit, Top Catal
327 2013;56(9) 714-24.
328 [23] Saka S, Dadan K. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel
329 2001;80:225-31.
330 [24] Kusdiana D, Saka S. Two-Step Preparation for Catalyst-Free Biodiesel Fuel Production. Appl
331 Biochem Biotech 2004;115(1-3):781-91.
332 [25] Minami E, Saka S. Kinetics of hydrolysis and methyl esterification for biodiesel production in
333 two-step supercritical methanol process. Fuel 2006;85(17-18):2479-83.
334 [26] Marker TL, Kokayeff P, Abdo SF, Baldiraghi F, Sabatino LMF. Production of diesel fuel from
335 biorenewable feedstocks with lower hydrogen consumption. US patent 2009/0193709 A1, 2009.

336 [27] Lestari S, Simakova I, Tokarev A, Mäki-Arvela P, Eränen K, Murzin DY. Synthesis of Biodiesel
337 via Deoxygenation of Stearic Acid over Supported Pd/C Catalyst. Catal Lett 2008;122:247–51.
338 [28] Standard Methods for the Analysis of Fats, Oils and Related Materials, 2.4.2.2-2013, Fatty acids
339 composition (FID temperature programmed gas chromatography), Japan Oil Chemists' Society,
340 Tokyo, 2013.
341 [29] ASTM D1298-99 Standard test method for density, or API gravity of crude petroleum and liquid
342 petroleum prducts by hydrometer method.
343 [30] ASTM D974-06 Standard Test Method for Acid and Base number by color-indicator titration.
344 [31] ASTM D1959-97 Standard test method for iodine value of drying oils and fatty acids.
345 [32] Maier W, Roth W, Thies I, van Ragué Schleyer P. Gas phase decarboxylation of carboxylic acids.
346 Chem Ber 1982;115:808-812.
347 [33] Mäki-Arvela P, Kubičková I, Snåre M, Eränen K, Murzin DY. Catalytic deoxygenation of fatty
348 acids and their derivatives. Energ Fuel 2007;21:30-41.
349 [34] Kubičková I, Snåre M, Eränen K, Mäki-Arvela P, Murzin DY. Hydrocarbons for diesel fuel via
350 decarboxylation of vegetable oils. Catal Today 2005;106:197–200.
351 [35] Simakova I, Rozmysłowicz B, Simakova O, Mäki-Arvela P, Simakov A, Murzin DY. Catalytic
352 Deoxygenation of C18 Fatty Acids Over Mesoporous Pd/C Catalyst for Synthesis of Biofuels. Top
353 Catal 2011;54(8-9):460–6.

354 [36] Snåre M, Kubičková I, Mäki-Arvela P, Eränen K, Murzin DY. Heterogeneous Catalytic
355 Deoxygenation of Stearic Acid for Production of Biodiesel. Ind Eng Chem Res
356 2006;45(16):5708-15.

357 [37] JIS K2204, Japanese industrial standards committee. Diesel fuel; 2007 [in Japanese].

List of figures

Figure 1: Schematic diagram of the saturated hydrocarbon production process via saturated fatty acids from rapeseed oil.

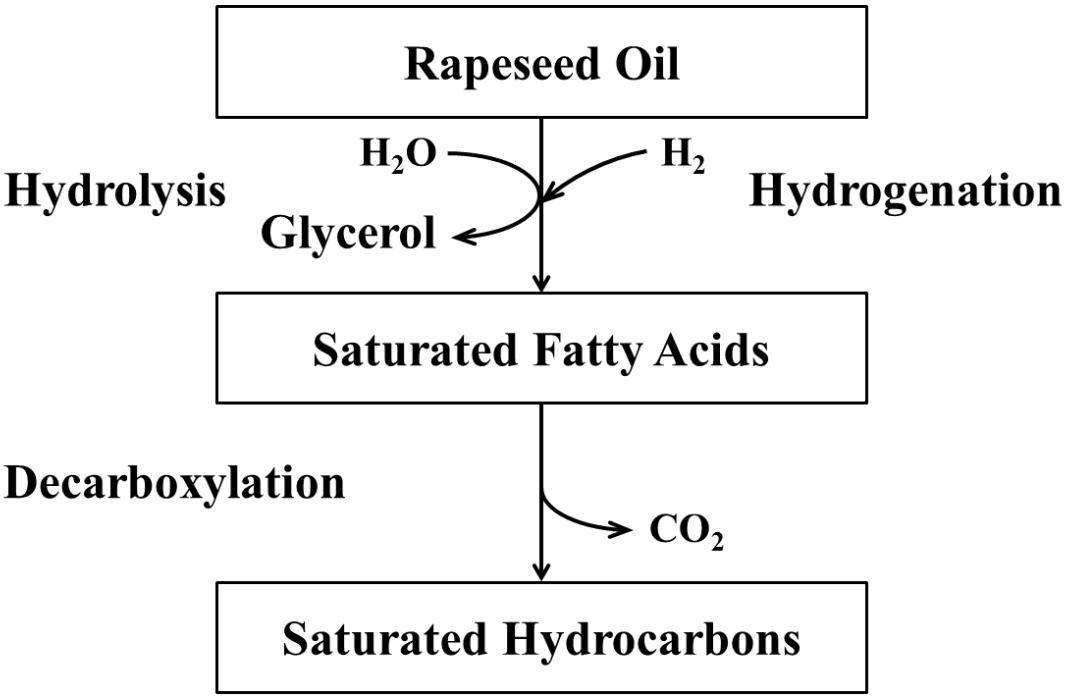
Figure 2: GPC (a) and HPLC (b) chromatograms of the obtained saturated fatty acids by hydrolysis/hydrogenation from rapeseed oil at 270 ºC/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C.

Figure 3: HPLC chromatograms of rapeseed oil, the obtained saturated fatty acids by hydrolysis/hydrogenation (270 ºC/ 5 MPa (H2) with 3.0 g of water and 0.05 g of Pd/C for 60 min) and the saturated hydrocarbons by decarboxylation (300 ºC/ 1 MPa (H_2) with 0.45 g Pd/C for 120 min).

List of tables

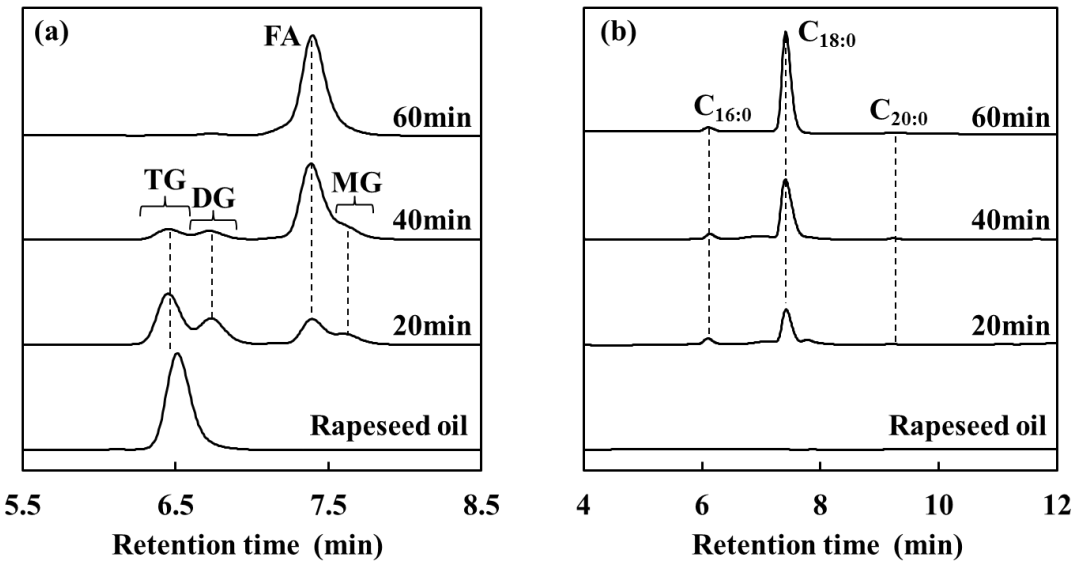
Table 1: Fatty acid composition of rapeseed oil, the obtained saturated fatty acids by hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation.

Table 2: The fuel properties of renewable diesel blended with fossil diesel in various ratios compared with Japanese #1 diesel standard (JIS K2204) [37].



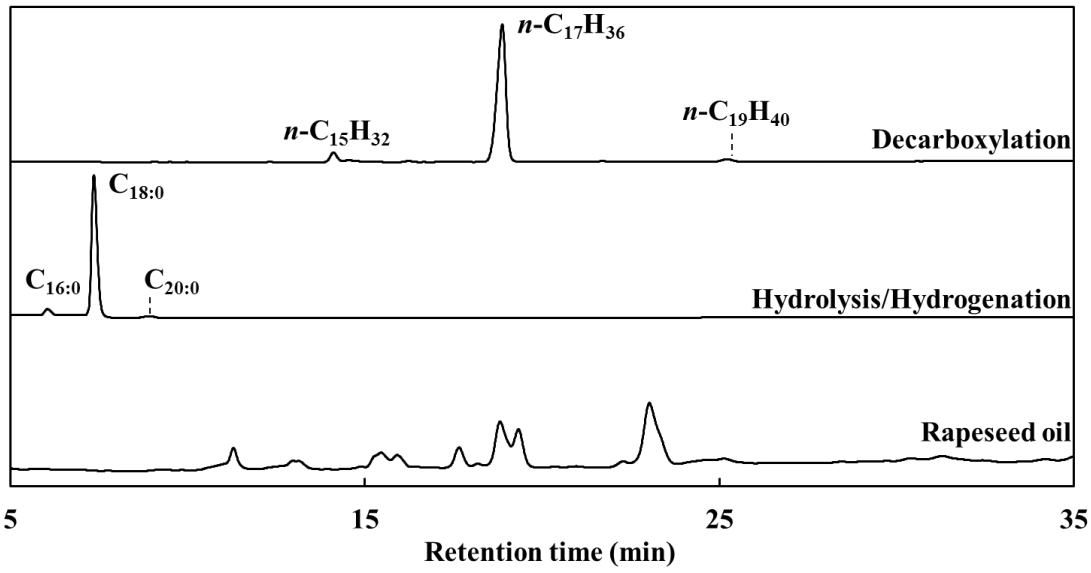
Fuel

Figure 1



Fuel

Figure 2



Fuel

Figure 3

Table 1: Fatty acid composition of rapeseed oil, the obtained saturated fatty acids by hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation.

		Yield (mol%)[*1]		
Fatty acid composition of rapeseed oil (mol%)		**Saturated fatty acids by hydrolysis/hydrogenation[*2]**	**Saturated hydrocarbons by decarboxylation[*3]**	
$C_{16:0}$	**4.3**	**4.5 (4.6)**	**4.1 (4.5)**	**$C_{15}H_{32}$**
$C_{16:1}$	**0.2**	**0.0**	**-**	
$C_{18:0}$	**0.7**	**89.7 (91.2)**	**85.7 (93.6)**	**$C_{17}H_{36}$**
$C_{18:1}$	**66.4**	**0.0**	**-**	
$C_{18:2}$	**19.4**	**0.0**	**-**	
$C_{18:3}$	**7.5**	**0.0**	**-**	
$C_{20:0}$	**0.5**	**1.9 (1.9)**	**1.7 (1.9)**	**$C_{19}H_{40}$**
$C_{20:1}$	**1.0**	**0.0**	**-**	
Glycerides	**-**	**2.3 (2.3)**	**0.0**	
Total	**100**	**98.4 (100)**	**91.5 (100)**	

*1: The values in parenthesis indicate the mol% on the total yield basis of rapeseed oil.

*2: 270 ºC/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C for 60 min

*3: 300 ºC/ 1 MPa (H_2) with 0.45 g Pd/C for 120 min

Table 2: The fuel properties of renewable diesel blended with fossil diesel in various ratios compared with Japanese #1 diesel standard (JIS K2204) [37].

Property	**Ratio of renewable diesel [*1] to #1 fossil diesel (vol%)**					**#1 diesel standard**
	100	**30**	**20**	**5**	**0 [*2]**	
Flash point (ºC)	**153**	**75.0**	**69.5**	**64.5**	**63.5**	**≧50**
Pour point (ºC)	**20**	**3.0**	**-2.5**	**-7.0**	**-8.0**	**≦-2.5**
Cold filter plugging point (ºC)	**22**	**-2.0**	**-6.0**	**-3.0**	**-5.0**	**≦-1**
Kinematic viscosity at 30 ºC (mm^2/s)	**4.5**	**3.7**	**3.6**	**3.6**	**3.5**	**≧2.7**
Density at 15 ºC (g/cm^3)	**0.77**	**0.82**	**0.83**	**0.83**	**0.83**	**≦0.86**

*1: The renewable diesel is prepared by mixing pure hydrocarbons with the same molar ratio as in Table 1.

*2: Renewable diesel 0 vol% corresponds to fossil diesel 100 vol%.